CONVERSION OF BOVINE MANURE TO OIL

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INTRODUCTION

Agriculture is the biggest source of wastes in the United States. Livestock on American farms produce over 2 billion tons of manure each year (approximately 400 million tons of organic matter), and these animal wastes are becoming a pollution, odor, and health problem. Efforts are being made by the Bureau of Mines to develop better and more efficient disposal methods using pyrolysis (1) and combustion (2) techniques. Animal waste is also a vast, untapped potential energy source if it can be converted to fuel.

Organic solid wastes, including urban refuse, agricultural wastes, sewage sludge, and bovine manure can be converted to oil by reaction with carbon monoxide and water at temperatures of 350° to 400°C and pressures near 4000 psig (3,4). The present work deals more extensively with the conversion of bovine manure to oil, and investigates effects of using synthesis gas (H_2:CO = 0.9:1) or hydrogen in place of carbon monoxide, and of adding catalyst and vehicle. It shows that synthesis gas can be used in place of carbon monoxide to convert manure to oil in reasonably good yield. Significant process improvements, such as low operating pressure and less energy requirement for heating, are achieved by the use of water:manure ratio as low as 0.25:1 with a suitable high boiling vehicle.

EXPERIMENTAL

The conversion of manure to oil with carbon monoxide and water was studied in a 1-liter magnetically-stirred stainless steel autoclave. Bovine manure from three sources was used. In the temperature range of 300° to 400°C, the operating pressure ranged from 2400 to 5300 psi. Most of these experiments were carried out for 0.5 to 1 hour at the reaction temperature. After the experiment, rapid internal cooling of autoclave to ambient temperature was achieved. Gaseous products were analyzed by mass spectrometry, and heavy oil products containing residue were separated from water and extracted by benzene to determine the amounts of the oil and the residue. The conversion of organic matter in manure was obtained by subtracting the weight percent of residue (excluding ash) from 100. Data on oil yield and carbon monoxide consumption were given on the basis of moisture-ash-free manure.

No catalyst was added for the conversion of manure with carbon monoxide and water. But in some runs using hydrogen or synthesis gas (H_2:CO = 0.9:1) in place of carbon monoxide, hydrogenation catalysts were used in an attempt to improve oil yield and hydrogen utilization.

RESULTS AND DISCUSSION

As shown in Table 1, both conversion and oil yield increased with temperature in the 300° to 380°C range, and the organic matter in bovine manure was almost completely converted by the reaction with carbon monoxide and water at 380° and 400°C. The variation in carbon monoxide consumption correlates well with the oil yield as shown in Figures 1 and 2 and is in the range of 0.7 to 0.8 gram/gram manure at the best conversion. Figure 2 also shows that there is no increase in oil production or carbon monoxide consumption after 15 minutes reaction time at 380°C. The unconverted residue was inorganic, mostly silica. The extent of gas evolution owing to the thermal decomposition of manure appeared to be minor based on carbon balance in the gas phase, but the net weight increase in the gas phase amounted to as much as 37 weight percent on the organic manure basis at 400°C, because of the oxygen removal from manure to form carbon dioxide and concurrent water-gas shift reaction to form carbon dioxide and hydrogen. In addition, substantial amounts of water-soluble compounds were present in the yellowish water layer. On standing in the air, the solution darkened and a precipitate formed. The aqueous solution was evaporated to dryness and the residue was analyzed by infrared spectroscopy. Strong bands in the 1600 cm^{-1} region (corresponding to formates and acetates) were observed.

TABLE 1. Effect of temperature on conversion of bovine manure (maf basis)

(manure[a] as received 40 g, water 160 g, 600 psi initial CO pressure, 1 hour reaction time)

Temp, °C	Operating pressure, psi	Conversion, percent	Oil yield, percent	Weight increase in gas phase, percent of manure	CO consumption, g/g manure
300	2440	79	14	20	0.13
350	3650	95	30	25	0.41
380	4780	99	38	35	0.70
400[b]	5300	99	38	37	0.81

[a] For analysis of manure, see Table 2.
[b] Reaction time is 30 minutes.

The analysis of manure and its products in Table 2 shows that treatment of manure with carbon monoxide and water results more in oxygen removal than in hydrogen addition. The hydrogenation effect is not apparent from the product analysis, because the starting manure probably contains many hydroxyl groups which contribute to the hydrogen content. Elemental analysis of the oil product did not vary significantly between 300° and 400°C. The oil product obtained at 380°C has a softening point below room temperature, a kinematic viscosity in the range of 520 to 580 centistokes at 60° C, and a heating value of 16,240 Btu per pound.

TABLE 2. Analysis of bovine manure and oil products, percent

	Manure[a]		Oil			
	As used[b]	maf basis	400°C	380°C	350° C	300°C
C	41.2	52.0	79.8	80.4	79.5	77.4
H	5.7	6.7	9.1	9.4	9.5	9.8
N	2.3	2.9	2.7	3.0	3.1	2.9
S	0.3	0.3	0.20	0.26	0.24	0.27
O (by diff.)	33.3	38.1	8.2	7.1	7.7	9.6
Ash	17.2	--	--	--	--	--
H/C atomic ratio		1.55	1.37	1.40	1.43	1.52

[a] Cow manure, Midwest Research Institute, Kansas City, Missouri.
[b] Moisture = 3.6 percent.

Use of hydrogen in place of carbon monoxide decreased the conversion and oil yield (Table 3). Synthesis gas (H_2:CO = 0.9:1) gave almost complete conversion but slightly lower oil yield than pure carbon monoxide, at a considerable reduction in the consumption of carbon monoxide. Some hydrogenation catalysts were used in an attempt to promote the utilization of hydrogen present in the gas phase. Cobalt molybdate appeared to have a favorable effect on the conversion of manure with hydrogen, but not when synthesis gas was used. When sodium carbonate was used with synthesis gas, a significant improvement in oil yield was obtained. An increase in autoclave pressure was also observed, indicating a greater degree of water-gas shift reaction as a result of the addition of sodium carbonate.

At a temperature of 450°C, significant improvements in oil product quality were observed in that the carbon content was increased, oxygen content was decreased, and viscosity was reduced (Table 4). The change in the oil product properties is accompanied by some decrease in the oil yield, mainly because the oxygen-containing groups are further reduced and/or removed. At this temperature, cobalt molybdate catalyst appears to have a beneficial effect in reducing the viscosity of the oil product. Hydrogen gave a more fluid product than synthesis gas.

The organic matter of manure contains about 40 percent oxygen which during the conversion process will be removed in the form of carbon dioxide, water, and water-soluble compounds. Based on our experience, we speculate that at best an oil yield of about 50 percent can be realized. Above experiments using water and carbon monoxide or synthesis gas have shown that the oil yield from manure is reasonable.

Water functions both as the reactant and vehicle. Water is the least expensive vehicle, but it has two economic disadvantages in a commercial process (1) operating pressure can become too high because of the high vapor pressure of steam at the reaction temperature, and (2) a large amount of energy is required to heat and vaporize water. Some experiments were carried out using only small amounts of water in the presence of a low-vapor pressure and less energy-requiring vehicle. An alkylnaphthalene-based oil (boiling above 235°C) was used as the vehicle. The results in Table 5 indicate that the water:manure ratio can be reduced to as low as 0.25:1 while giving 83 percent oil product yield based on feed of maf manure plus vehicle. As discussed earlier, if one assumes that only 50 percent of organic matter in manure can be converted to oil, the maximum obtainable oil product yield based on maf manure plus vehicle would be 87.5 percent. If we assume a 98 percent recovery for the vehicle as we found in a blank run, the above 83 percent yield based on feed would be equivalent to 38 percent oil yield based on maf manure. The operating pressure is also reduced significantly as the water:manure ratio is decreased. This reduction in pressure and use of a vehicle oil (generated in the process) significantly decrease the high capital investment and operating cost of the manure to oil process.

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TABLE 3. Effects of hydrogen or synthesis gas[a] on conversion

(160 g water, 40 g manure as received, 2 g catalyst, 600 psi initial pressure, 1 hour at 380°C)

Gas	Catalyst	Operating pressure, psi	Conversion, percent	Oil yield, percent	Weight increase in gas phase, percent of manure	CO consumption, g/g manure
H_2	--	4500	83	21	18	--
H_2	$SnCl_2$	4360	81	22	19	--
H_2	CoMo	4540	90	27	22	--
H_2 + CO	--	4740	99	34	30	0.41
H_2 + CO	CoMo	4680	99	33	28	0.40
H_2 + CO	Na_2CO_3	4790	99	38	35	0.48
H_2 + CO	CoMo + Na_2CO_3	4770	99	38	35	0.47

[a] H_2:CO = 0.9:1.

TABLE 4. Conversion of steer manure[a] at 450°C (maf basis)

(reaction time = 0.5 hour)

Gas	H_2	$H_2 + CO$[b]	$H_2 + CO$[b]
Water:manure	0:1	1:1	1:1
Catalyst[c]	CoMo	CoMo	--
Operating pressure, psi	3700	4150	4200
Conversion, percent	99	99	99
Oil yield, percent	15	22	21
Oil analysis,			
C	85.3	82.6	81.3
H	8.8	8.4	8.5
N	3.6	6.0	6.9
S	0.33	0.33	0.24
O (by diff.)	1.97	2.67	3.06
H/C atomic ratio	1.24	1.22	1.25
Kinematic viscosity of oil at 60°C, centistoke	10	133	252

[a] Texas steer manure; analysis, percent: C = 25.5, H = 4.0, N = 2.6, S = 0.4, O = 22.8, ash = 44.7, moisture = 5.7.
[b] $H_2:CO = 0.9:1$.
[c] 3.3 parts per hundred parts manure.

TABLE 5. Effect of vehicle

(1000 psi initial synthesis gas[a] pressure, 380° C)

Water:manure[b]:vehicle[c]	1:1:2.5	0.5:1:2.5	0:25:1:2.5	0.25:1:2.5
Catalyst	--	--	Na_2CO_3	--
Operating pressure, psi	3400	3100	2800	3300[d]
Time, hr	0.5	0.5	1	0.5
Conversion, percent	94	91	95	89
Oil product yield, percent feed[e]	84	83	83	82

[a] $H_2:CO = 0.9:1$.

[b] Beef cattle manure, Beltsville, Md.; analysis, percent: C = 44.7, H = 6.4, N = 3.0, S = 0.37, O = 37.2, ash = 8.3, moisture = 5.9.
[c] An alkylnaphthalene-based oil, Sunoco.
[d] 1260 psi initial pressure.
[e] Based on feed of maf manure plus vehicle.

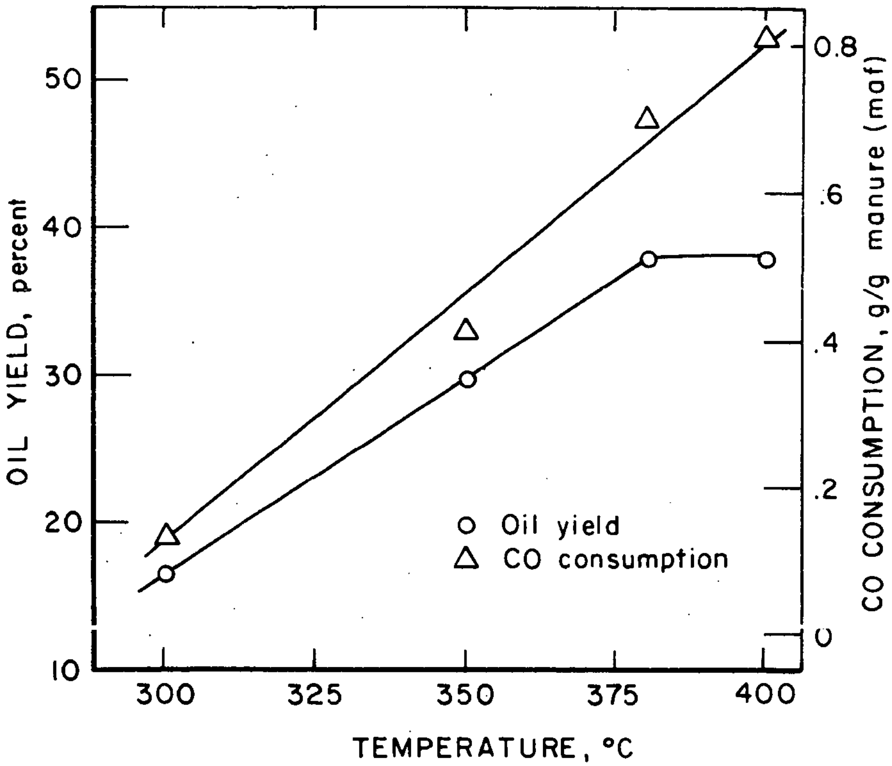

Figure I - Effect of temperature on oil yield and CO consumption at I hour reaction time.

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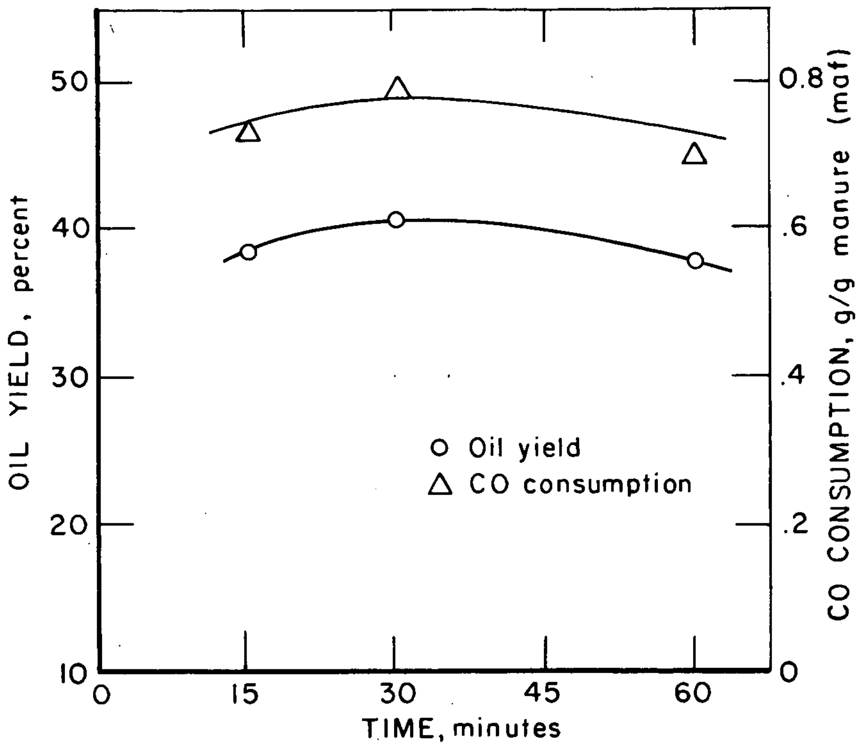

Figure 2 – Effect of reaction time on oil yield and CO consumption at 380°C.

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